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SUBSTRATE INDUCED ORDERING OF MOLECULAR ADSORBATES ON Au(111)

by

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SUBSTRATE INDUCED ORDERING OF MOLECULAR ADSORBATES ON Au(111)

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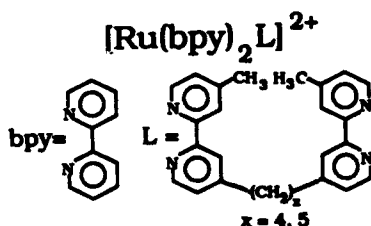
Abstract. Adsorbed monolayers of $\text{Ru}(\text{bpy})_2\text{bpy}-(\text{CH}_2)_x-(\text{bpy})^{2+}$ ($x = 4$ and 5) on the unreconstructed and $\sqrt{3} \times 22$ reconstructed surfaces of Au(111) were imaged by scanning tunneling microscopy in dimethylformamide. On the reconstructed surface, the adsorbed films display highly-ordered patterns that are commensurate with the measured corrugation patterns of the substrate. In contrast, when adsorption is on the atomically smooth unreconstructed surface, STM images reveal a random spatial distribution of $\text{Ru}(\text{bpy})_2\text{bpy}-(\text{CH}_2)_x-\text{bpy}^{2+}$.



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We report scanning tunneling microscopy (STM) in dimethylformamide (DMF) of monolayers of $[\text{Ru}(\text{bpy})_2\text{bpy}-(\text{CH}_2)_x\text{-bpy}^{2+}]^1$, *I*, ($\text{bpy}-(\text{CH}_2)_x\text{-bpy}$ is an α,ω -bis(4'-methyl-2,2'-bipyridyl-4-yl)alkane and x , the number of methylene groups in the alkane chain is either 4 or 5) adsorbed on the unreconstructed and $\sqrt{3} \times 22$ reconstructed surfaces



of Au(111). The key finding of our study is that the observed supramolecular structures of electroactive films of *I* (for $x = 4, 5$) on the $\sqrt{3} \times 22$ reconstructed surface are commensurate with the long-range atomic corrugation of the underlying substrate. In contrast, long-range ordering is absent in films of *I* adsorbed on the unreconstructed and atomically flat Au(111) surface. The results suggest that the adsorption of *I*, through interactions of the pendant bipyridyl group with the Au atoms, is modulated in real space with a periodicity of $\sim 30\text{\AA}$. Several previous STM studies have focused on the specific orientation and/or location of adsorbates with respect to the substrate's atomic structure²⁻⁴. The present work demonstrates that variations in the electron density at a surface, which occur as a result of a reconstruction, can dictate the structural features of an adsorbate layer.

The study of Au(111) has received a great deal of attention from STM researchers in recent years. Atomically flat, clean surfaces can be prepared in UHV and in ambient environments and atomic corrugation can be measured in UHV⁵, air⁵, and liquids⁶. A particularly interesting feature of the Au(111) surface, which will play a major role throughout this report, is its reconstruction. Au(111) is the only fcc (111) metal surface known to reconstruct, as established by a number of surface sensitive techniques⁷⁻⁹. However, the exact atomic positions within the unit cell of the reconstructed surface and the new long-range features of this reconstruction were revealed only recently in an ultrahigh

vacuum STM study by Barth et al.¹⁰. Haiss et al.⁶, subsequently demonstrated that this information could also be obtained with the sample being exposed to air or organic solvents. Generally, reconstructions result in surface layer atomic and electronic distributions which differ, sometimes markedly, from an ideally bulk terminated lattice. Thus, it is expected that the adsorption and nucleation behavior of monolayer quantities of adsorbed species may reflect these variations. Indeed, Chambliss et al.¹¹ demonstrated in a recent STM study that submonolayer quantities of Ni adatoms nucleate on the reconstructed Au(111) surface in a pattern which reflects topographical features of the underlying reconstruction.

The $\sqrt{3} \times 22$ phase can be obtained by thermal annealing of the Au(111) surface or by a tip-induced electronic transition as previously described¹². Fig. 1 shows a typical STM image of the $\sqrt{3} \times 22$ reconstruction obtained in our laboratory^{13,14}. The reconstructed surface is imaged in STM as parallel pairs of corrugation lines with a horizontal pair-to-pair separation of $\sim 65\text{\AA}$ and a vertical corrugation amplitude of $\sim 0.2\text{\AA}$. The spacing between corrugation lines within a pair is $20\text{-}25\text{\AA}$. Barth, et al., have shown that each corrugation line on the bare, reconstructed surface marks a transition between hexagonal close packed and face centered cubic stacking regions. Parallel line pairs can either extend over several hundreds of angstroms (i.e. the area to the right in Fig. 1), crossing, apparently unperturbed, monoatomic steps (not shown here). In addition, line pairs are organized in domains, separated by $\sim 250\text{\AA}$ and rotated by $\pm 120^\circ$ with respect to each other, i.e., the zig-zag "herringbone" pattern, which can also be seen in Fig. 1. Similar surface features have been observed by many groups in various sample environments: UHV¹⁰, air^{6,12}, polar organic solvents⁶ and electrolytes¹⁶. In contrast, images of the unreconstructed Au(111) surface show the normal hexagonal arrangement of Au atoms (2.9\AA spacing), but none of the features described above.

Fig. 2 shows images of Au(111) surfaces in DMF solutions containing $\sim 0.5\text{ mM}$ *I*. Reconstructed Au(111) samples (after thermal annealing) immersed in DMF solutions

containing $I(x=5)(PF_6^-)_2$ exhibit the structure shown in Fig. 2a. The image in Fig. 2b was obtained after immersing unreconstructed Au(111) samples in DMF solution containing $I(x=4)(PF_6^-)_2$. The difference between the image in Fig. 2a and the one in 2b is striking. Ordered rows of quasi-spherical entities ($\sim 10\text{-}13\text{\AA}$ radii) with $\sim 30\text{\AA}$ periodic spacing decorate the reconstructed surface, whereas random structures appear on unreconstructed samples. Evidence that all of these structures are due to molecular adsorption comes from the following: 1) all of the observed patterns are highly reproducible with different tips and different samples; 2) similar adsorption patterns are observed for I comprised of longer ($x = 12$) and shorter ($x = 2$) methylene linkages; 3) preliminary voltammetry studies show that $I(x = 5)$ adsorbs on Au(111) surfaces as evidenced by the fact that a voltammetric wave can be observed in acetonitrile/0.1 M tetra(n-butyl)ammonium perchlorate (TBAP) at about +1.23V (vs. saturated calomel electrode) following immersion of a gold-electrode in a DMF solution containing $I(x=5)$ and after rinsing with acetone; and, 4) a detailed STM investigation of the bare Au(111) surface immersed in DMF solutions without I reveals that none of the structures shown in Figs. 2 are due to DMF. These studies will be published elsewhere.

In Fig. 3, we show topographical profiles across the (a) bare $\sqrt{3} \times 22$ surface and (b) a $\sqrt{3} \times 22$ on which $I(x=5)$ is adsorbed. The profiles are measured normal to the direction of the corrugation lines. The profiles show that the periodicity of the pair-to-pair line separation for the bare surface and monolayer are essentially equivalent (69 ± 7 vs $73 \pm 14\text{\AA}$). The intrapair line spacing is larger on surfaces covered with $I(x=5)$ ($35 \pm 9\text{\AA}$) than on the bare surface ($21 \pm 4\text{\AA}$). The height corrugation (z direction) of the $\sqrt{3} \times 22$ surface modified with $I(x=5)$, $7\text{-}10\text{\AA}$, is $\sim 35\text{-}50\times$ larger than on the bare surface (0.2\AA), but less than expected if the methylene chain were fully extended ($\sim 15\text{\AA}$). This might suggest that the chains are not fully extended, perhaps in order for the molecules to minimize electrostatic repulsions. Such an effect has been previously proposed for related complexes¹⁷. However, currently there is little understanding of electron tunneling through

adsorbed molecular layers. Thus, height measurements of such layers are more of a qualitative nature.

Based on the qualitative and quantitative similarities between the corrugation patterns for the bare and reconstructed Au surface (Fig. 1) and those observed in images of films of *I* on the same surfaces (Fig. 2 a), we propose that the chemical reactivity of the reconstructed Au(111) towards adsorption of *I* is spatially modulated by periodic electronic and/or topographic features of the substrate. The pattern observed in Fig. 2a can thus be rationalized by assuming that *I* adsorbs preferentially on sites in the transition region between hcp and fcc stacking regions (i.e., the corrugation lines, vide supra), Fig. 3. In such a model, row pairs of molecules should be observed in the images with a pair-to-pair separation of $\sim 65 \text{ \AA}$, and separation of individual rows (within a pair) of $\sim 30 \text{ \AA}$, in excellent agreement with our experimental observations. A full account of our study will be reported in the near future.

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Figure Captions.

1. Representative STM image of the $\sqrt{3} \times 22$ reconstructed Au(111) surface. (Set-point bias, V_b , and tunnel current, i_t : ($V_b = -100$ mV; $i_t = 4.2$ nA)

2. STM images of: (a) $I(x = 5)$ on the $\sqrt{3} \times 22$ Au(111) reconstruction; (b) $I(x = 4)$ on the unreconstructed Au(111) surface. All images obtained in DMF containing ~ 0.5 mM of I . Set-point bias and tunnel current: (a) $V_b = -92$ mV; $i_t = 4.5$ nA; (b) $V_b = -100$ mV; $i_t = 3.8$ nA)

3. Variation of the tunneling current across the $\sqrt{3} \times 22$ Au(111) surface (a) before and (b) after immersion in a DMF solution containing ~ 0.5 mM $I(x = 5)$. (c) Schematic drawing of the proposed monolayer structure on the $\sqrt{3} \times 22$ Au(111) surface.

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13. A Nanoscope II Scanning Tunneling Microscope was used with mechanically cut Pt/Rh (70/30) tips. All images were recorded in the constant current mode at a scan rate of 8.6 Hz.
14. Au surfaces were prepared according to the procedure of Hsu and Cowley (15): a 2 cm length of 99.999% 0.5 mm diameter Au wire was flame cut; Au spheres (1-2 mm diameter) were formed by heating one end of the wire in a H_2/O_2 flame until molten. Upon cooling in Ar or air, highly reflective, optically flat facets appear on the surface. Spheres that were not further annealed typically displayed large atomically flat unreconstructed areas on the facet in STM images. Spheres annealed in a cooler H_2/O_2 flame typically exhibited large reconstructed areas.
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2/20/92

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February 27, 1991

Professor Israel Wachs
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Dear Professor Wachs,

From my correspondence with Professor Humphrey, I learned that your Department has an ongoing search to fill in two faculty positions. I am also aware that the process is already well underway. I would be very pleased indeed if the Search Committee could review my application under these circumstances. Thank you very much for your time and consideration.

Sincerely yours,

Hugo Vits

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